Investigating anharmonicity using molecular dynamics calculations: The TM hydride series (PH3)3MH4, (M = Os, Ru and Fe)

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Investigating anharmonicity using molecular dynamics calculations: The TM hydride series $(PH_3)_3MH_4$, (M = Os, Ru and Fe)**†

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[†]Dedicated to Professor David W. H. Rankin on the occasion of his retirement.

Synopsis:
We have performed ab initio MD simulations on $(PH_3)_3MH_4$ (M = Os, Ru and Fe) to quantify the effects of anharmonicity in refining diffraction data sets and interpreting vibrational spectra.

Keywords:
Transition-metal hydrides, *ab initio* molecular dynamics, anharmonicity

Abstract

We present an *ab initio* molecular dynamics study of the iron triad complex $(PH_3)_3MH_4$, (M = Os,Ru and Fe). We calculate numerical atomic probability density functions (PDFs), which offer direct visualisation of the degree of anharmonicity present in these complexes. Fitting our calculated PDFs to a parabolic transformation of the standard crystallographic ellipsoidal PDFallowed the bond correction for librational motion observed in the M–H distances to be obtained. For the Ru and Fe complexes we also attempt to quantify the bond distance correction needed to describe the η^2-bound H_2 ligand anharmonically. From our simulations we also obtain anharmonic vibrational spectra, which we compare to experimental data. Finally, we also comment on a spontaneous $H_2/(H)_2$ ligand flipping process observed for the Fe complex.

I. Introduction

The first report over 30 years ago of a transition-metal (TM) complex that could bind intact molecular hydrogen gave rise to a wealth of scientific activity that continues to this day.[1-6] There was a drive to rationalise the structures, bonding and chemical reactivities of these unusual chemical species. Today complexes of this type are employed in many catalytic processes due to their ability to activate small molecules and cleave strong non-polar bonds.

The existence of the η^2-bound dihydrogen ligand, rather than the classical hydride form (see Fig. 1), had been suspected for some time before the first definitive report.[1] The species was first thought to exist transiently as a reactive intermediate, but anomalies in the infra-red (IR) vibrational frequencies gave the first clues that the new bonding interaction was actually quite stable. Diffraction (X-ray and neutron) studies were often frustratingly hampered by disorder which prevented full structural refinements. In the end it was spectroscopic evidence (^{1}H NMR and Raman) that finally allowed Kubas *et al.* to claim η^2-H_2 binding to a TM centre.

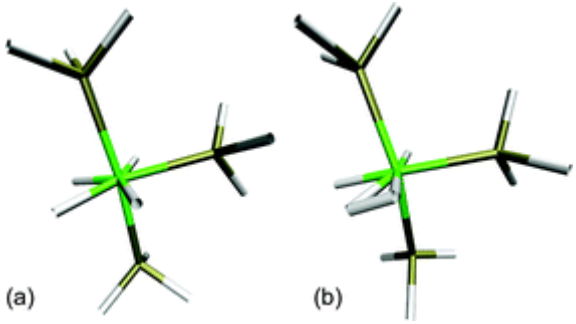

Figure 1. The molecular structure of $(PH_3)MH_4$, showing (a) the classical hydride and (b) the dihydrogen ligand complex geometries.

The dihydrogen ligand complexes are highly anharmonic, which forms the primary interest for this study. The IR stretching frequency for the η^2-H_2 ligand is a very weak signal and has been recorded over the range from 2400 to 3100 cm^{-1},[6] compared to 4300 cm^{-1} for free H_2. Anharmonic systems are challenging to study as they expose the underlying approaches made in defining structural parameters by different techniques, and some rather dramatic disagreements can occur.[7] For instance, a computed optimised structure refers to the vibration-free structure at the global minimum of the potential-energy surface. However, in reality of course atoms are not static but oscillate around mean positions. If the system is harmonic then the equilibrium and mean positions will coincide; any degree of asymmetry and they will not. Thus we could reasonably expect that a standard *ab initio* optimised structure may differ from an experimental structure to a significant degree.

Crystallography is the gold-standard technique employed to define molecular structure in the solid state. Here, the thermal motion of each atom is accounted for using the Debye–Waller factor,[8] which is the reciprocal-space form of the real-space three-dimensional probability density function (PDF). The mean of the PDF corresponds to the atomic position that is refined in the data fitting process. Depending on the form of PDF employed a different position based on the maximum of the probability density can be defined.[9] The majority of crystal structure determinations utilise harmonic, trivariate Gaussian PDFs (more commonly known as ellipsoids), which are described by six parameters: three to define the dimensions of the ellipsoid and a further three to define its orientation.

It is important to appreciate, however, that the standard ellipsoidal/Gaussian PDF may not be sufficient to describe highly anharmonic systems. Moreover, unless thediffraction data set is large enough to encapsulate diffuse scattering, a so-called total-scattering analysis, then all information on atomic correlation (*i.e.* how the motion of any one particular atom affects the others) is lost.[10] Normally, the loss of this information does not present too many issues, but in the case of highly anharmonic systems it is crucial. One well-known example is librational motion, where *e.g.* treating the rotation of a light atom around a heavy atom harmonically gives rise to an apparent shortening of the bond distance.[11] Thus inappropriate treatment of the atomic PDFs can give rise to systematic errors in bond distance parameters, which may be very significant depending on the degree of anharmonicity present. For the TM hydride series it is reasonable to expect that the M–H bond distances will display librational motion and hence the values returned by standard crystallographic practices are likely to be too short. Similarly, assuming harmonic behaviour for the η^2-H_2 ligand may also result in significant errors.

Returning to the computational perspective, the effects of anharmonicity on individual bond parameters can be investigated directly by molecular dynamics (MD) simulations. Here energy is added to the system and the forces on the atoms are calculated to propagate their positions on the classical surface for a short time interval. The forces are then recalculated, and the process is repeated for a large number of steps (resulting typically in a total time trajectory of tens of picoseconds), until the atoms have covered a representative region of space. The key factor for this work is that anharmonicity is automatically taken care of. Any bond distances extracted

from MD simulations will account for the atomic correlation for that pair of atoms, and Morse oscillatory behaviour should be observed. This means that any degree of anharmonicity in the underlying potential energy surface will result in the time-averaged bond distances being longer than their equilibrium structure counterparts. In addition, by mapping the individual frames from the MD simulation back to a common frame of reference, we can calculate numerical PDFs for comparison with the standard crystallographic ellipsoidal approach. We can also fit these calculated probability distributions to simple models that attempt to capture the anharmonicity, ideally using only a few additional parameters required to model the standard crystallographic PDFs. To this end we have recently reported on a new atomic PDF that attempts to capture the anharmonicity present due to vibrational motion along a curved trajectory.[12] The function is based on a parabolic transformation of the standard crystallographic ellipsoid and requires only two extra parameters to bend the distribution around two axes. Fitting our numerical PDFs to this function therefore allows us to derive a correction for bond lengths affected by librational motion in crystallographic studies.

Finally, anharmonic vibrational frequencies can also be extracted from MD trajectories by Fourier transformation of individual atomic velocity autocorrelation functions.[13] Thus we can plot the vibrational spectra for just the hydrogen atoms in the TM hydride complex, generating very clean spectra for comparison with experiment, an area which has also been fraught with challenges. It is also possible to extract vibrational information from individual geometric parameters (bond lengths, angles, *etc*.) obtained over the course of the trajectory to aid in the assignment of the vibrational modes.

In this work we present an *ab initio* MD study of a model system of the iron triad complex $(PH_3)_3MH_4$ (where M = Os, Ru or Fe), which constitutes one of the best known examples of a polyhydride system and has been the subject of several previous studies.[14-16] It is known that the Os derivative adopts the classical hydridestructure, whereas the Ru and Fe favour the dihydrogen ligand arrangement as their lowest energy configurations. From our trajectories we report time-averaged M–H and H–H bond distances and atomic PDFs which allow us to visualise directly the extent of the anharmonicity in these systems. Where possible we have fitted these distributions to our new curved distributions to obtain the librationally corrected M–H bond distances. We also attempt to quantify the error in the H–H bond distances if the system is modelled harmonically, as is done as standard in crystallographic refinements. We also report on the anharmonic vibrational spectra obtained for each member of the series and compare with experimental data where available. Finally, we comment on a spontaneous $H_2/(H)_2$ ligand flipping process which was observed for the Fe complex.

II. Computational methods

Starting coordinates for the $(PH_3)_3MH_4$ (where M = Os, Ru or Fe) system were placed in a cubic periodic boundary condition cell with dimension 15 Å. All simulations were run using the CP2K[17,18] molecular

dynamics simulation package with the generalised-gradient-approximation functional PBE[19] coupled to a dual localised (Gaussian) and plane-wave basis set description. The localised basis sets employed[20] were a mixture of double-zeta (for the metal) and triple-zeta (for the phosphorous and hydrogen) quality and optimised for use against the Goedecker-Teter-Hutter set of pseudopotentials.[21] A series of single-point energy calculations determined the optimum energy cut-off (4080 eV), which converged the total energy to within 1 meV/atom. The subsequent geometry-optimisation calculations were performed using the Broyden-Fletcher-Goldfarb-Shanno (BFGS) method.[22-24] These equilibrium structures provided the starting points for MD simulations performed within the NVT ensemble (maintained at 350 K *via* a chain of Nose-Hoover thermostats;[25] note this temperature was chosen to minimise the impact of quantum tunnelling, which is not captured in this style of simulation), advancing in time increments of 0.55 fs until trajectories amounting to *ca.* 15, 20 and 30 ps were obtained for the Os, Ru and Fe systems, respectively.

III. Results and discussion

Equilibrium structures (0 K): The use of a plane-wave basis set dictates that a pure DFT functional, rather than one of the more popular hybrid functionals, must be employed in the simulations. However, a comparison with the optimised structure obtained for the Os complex at B3LYP/lanl2DZ (using the G03 simulation package[26]) showed that the optimised parameters were essentially the same, with *e.g.* all M–H bond lengths in agreement to within 0.005 Å.

There exists a low temperature neutron diffraction structure closely related to the $(PH_3)_3OsH_4$ complex [specifically, $(PhMe_2P)_3OsH_4$] that allows us to further assess the ability of the computational model to reproduce the main structural features for this type of complex.[27] We observe a close correlation between simulated and experimental values, with *e.g.* the Os–P bond distances calculated to fall within the range 2.29–2.33 Å (*cf.* exp. 2.31–2.35 Å), and both methods positioning the longest bond to lie in the equatorial plane. The three P–Os–P angles agree with the experimental values to within 3°. Similarly, the four Os–H distances (see Table 1) are calculated to lie over the same range of values as found experimentally (1.64–1.68 Å), and follow the same geometric trend, namely that the outermost Os–H distances are longer than the inner pair by around 0.03 Å. The non-bonding H···H distances (see Table 1) also fall over similar ranges (1.84–1.88 Å calculated, 1.84–1.91 Å experiment). We therefore conclude that our equilibrium structure for $(PH_3)_3OsH_4$ encapsulates the essential geometric features for this complex.

Table 1. Selected distances for the $(PH_3)_3MH_4$ series obtained from the equilibrium structures, the time-averaged interatomic distances and the time-averaged atomic positions

Parameter	**Equilibrium (0 K)**	**Time-averaged interatomic distances (350 K)**	**Time-averaged atomic positions (350 K)**
Os–H(1)	1.673	1.685	1.666
Os–H(2)	1.645	1.649	1.621
Os–H(3)	1.642	1.650	1.622
Os–H(4)	1.682	1.684	1.666
H(3)···H(4)	1.839	1.846	1.816
Ru–H(1)	1.633	1.640	1.563
Ru–H(2)	1.639	1.648	1.568
Ru–H(3)	1.772	1.779	1.653
Ru–H(4)	1.750	1.784	1.662
H(3)–H(4)	0.890	0.904	0.273
Fe–H(1)	1.520	1.523	1.499
Fe–H(2)	1.518	1.528	1.490
Fe–H(3)	1.581	1.600	1.521
Fe–H(4)	1.598	1.600	1.504
H(3)–H(4)	0.912	0.934	0.204

As anticipated, the heavy-atom equilibrium geometry for the $(PH_3)_3RuH_4$ complex neatly matches that observed for the Os complex, with the M–P distances in agreement to within 0.01 Å but the wide P–M–P angle narrows by nearly 10°. For the Fe complex there is also a neutron diffraction structure on a closely related complex $[(Ph_2EtP)_3FeH_4]$ against which we can assess our simulated structure.[15] The calculated Fe–P distances fall over the range 2.12–2.17 Å, compared to the experimental range 2.17–2.21 Å, with the longest bond again lying in the equatorial plane. The calculated P–Fe–P angles agree with their experimental counterparts to within 5°. The calculations correctly predict the non-classical dihydrogen form as the lowest energy arrangement for both the Ru and Fe complexes. This impacts on the M–H distances, with those involved with the η^2-bound ligand lengthening by around 0.1 Å. Agreement for these bond distances with the neutron diffraction study was to within 0.15 Å. The H_2 ligand sits tilted out of the equatorial plane by around 5° for both complexes. The heavy-atom framework bends away from the H_2 unit, with P–M–H angles for the dihydrogen unit for both complexes typically around 95°, compared to around 80° for the classical hydrogen atoms. This observation mirrors the experimental report for the Fe complex. Finally we note that the calculations return H–H contact distances of 0.890 and 0.912 Å for the Ru and Fe complexes, respectively [*cf.* 0.821(10) Å by experiment for the $(Ph_2EtP)_3FeH_4$ complex].

Time-averaged structures (350 K): The MD trajectories allow us to explore the local potential-energy landscape as the molecular geometry oscillates around its equilibrium position. Crucially, this is done in the absence of any harmonic constraints, and therefore allows us to extract time-averaged structural parameters

that will naturally encapsulate anharmonic behaviour. These results are presented in Table 1, where we observe that all time-averaged interatomic distances (obtained by extracting the distances directly from the MD simulation, and then averaged in accordance with the blocking method[13]) display standard Morse-curve oscillatory behaviour, meaning that the values obtained are longer than their equilibrium partners in every case. This is a clear indicator of the asymmetry inherent in these systems, since the time-averaged and equilibrium structure parameters should coincide in the case of a harmonic system. The extent of the bond lengthening is considerable, particularly for the Ru and Fe complexes, with bond distance corrections of the order of 0.02–0.03 Å observed in these cases. We also observe that for both complexes the H_2 ligand rotates almost freely around its equilibrium position, with both clockwise and anticlockwise torsional motion observed.

Atomic probability distribution functions (PDFs) (350 K): The numerical PDFs shown in Fig. 2 were obtained by mapping each molecular frame from the MD trajectory back to a common frame of reference and binning the resulting positions for the four hydrogen atoms connected to the central TM atom. The three images presented for each structure represent, in turn, a three-dimensional distribution, a two-dimensional isosurface [with the colour spectrum ranging from blue (high probability density) to red (low probability density)], and finally the same data fitted to a harmonic ellipsoid distribution set to a 50% probability level. The anharmonicity inherent in these systems can be clearly observed from these plots, with the hydrogen atoms following trajectories strongly influenced by librational motion. The resulting shrinkage effect is reflected in the data presented in the final column ofTable 1; here the atomic coordinates of the atoms over the course of the trajectory have been averaged, and then used to calculate the M–H and H–H bond lengths. As this process results in the loss of atom correlation we observe an appreciable shortening for all bond distances, which is particularly noticeable for the Ru and Fe complexes. Distances associated with the η^2-bound H_2 are the most strongly affected, shortening by around 0.1 Å compared to the equilibrium structure values. Thus to conclude for anharmonic systems preserving the correlation between atoms results in bond lengthening with respect to the equilibrium value; loosing the correlation results in bonds shortening.

We now turn to the task of fitting these numerical PDFs, which we achieve by first fitting to the standard six-parameter trivariate Gaussian distribution, and then performing a parabolic transformation of this distribution by the addition of just two further parameters.[12] By locating the most-probable position in this new anharmonic distribution we can determine the bond length correction that would account for the effects of librational motion in the crystallographic study. We start with the classically-bound hydrogen atoms, as these should conform well to this type of anharmonic PDF. The resulting fits are shown in Fig. 3–5. For the Os case the subsequent lengthening in the M–H bond is around 0.01 Å, which is just over 3σ of the experimental bond length determination, and is therefore a significant correction [see Fig. 3]. For the Ru and Fe complexes the degree of curvature observed is even more appreciable [see Fig. 2(b,c)]. We focus our attention on atoms H(2)

for these complexes, as the numerical PDFs obtained for atoms H(1) show a significant amount of tilting in addition to the librational curving. The resulting anharmonic fits are shown in Fig. 4(a) and 5(a), which give rise to a lengthening in the M–H(2) bond distances by around 0.02 Å. This again amounts to just over a 3σ correction compared to the experimental bond length determination measured for $(Ph_2EtP)_3FeH_4$.

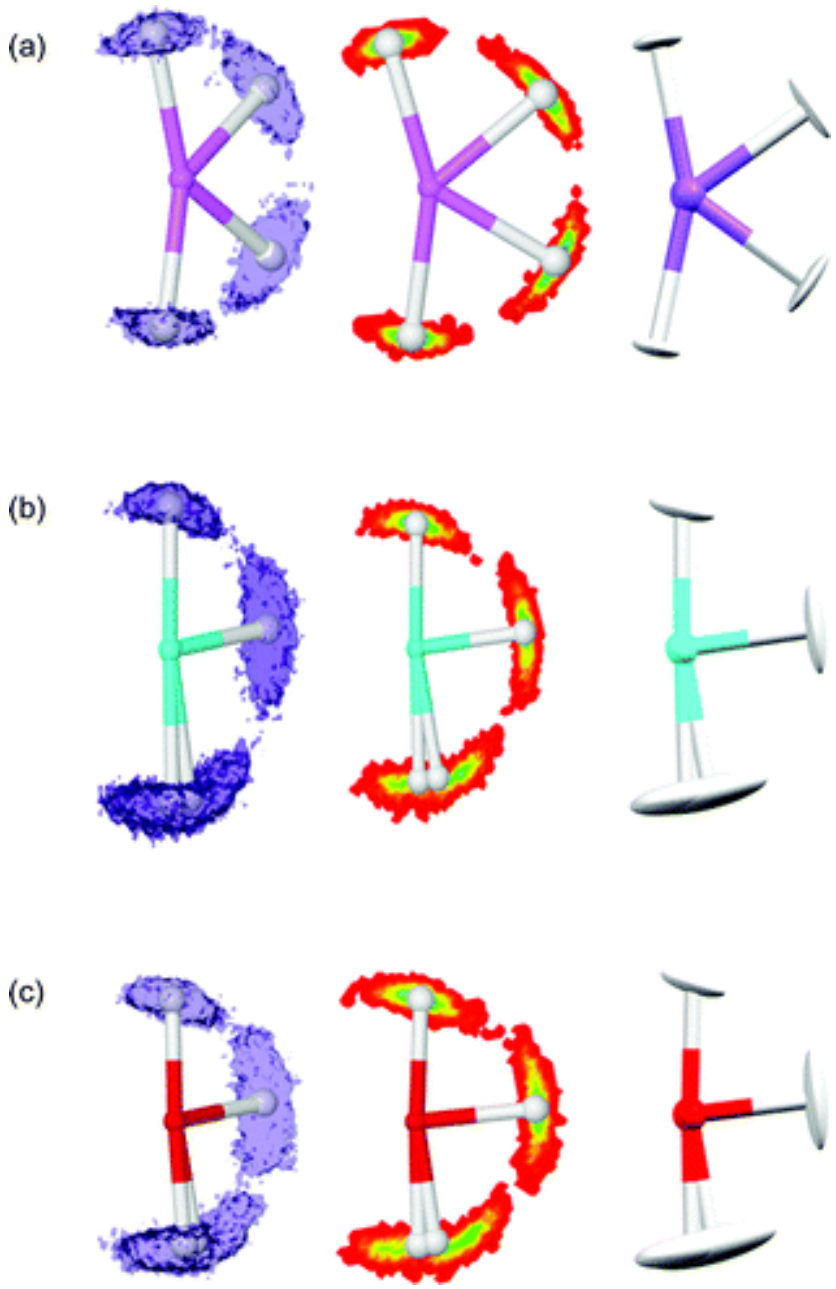

Figure 2. Calculated atomic PDFs for the hydride atoms in (a) $(PH_3)_3OsH_4$, (b) $(PH_3)_3Ru(H_2)H_2$ and (c) $(PH_3)_3Fe(H_2)H_2$. The hydrogen atom numbering scheme H(1) to H(4) runs from the top in a clockwise direction.

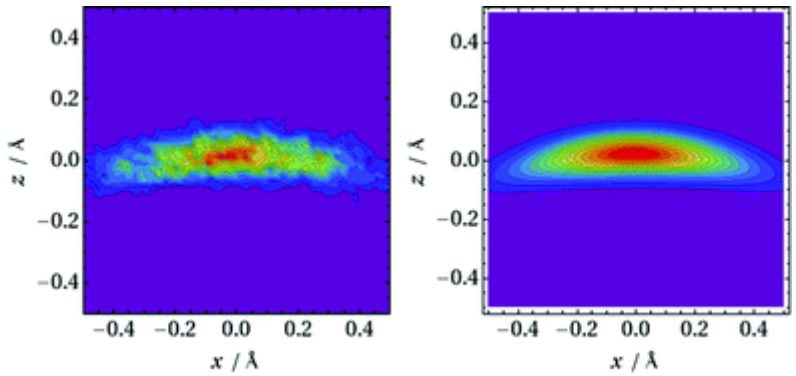

Figure 3. Numerical PDFs for a hydride atom in $(PH_3)_3OsH_4$, obtained from the MD trajectory (left) and fitted to a parabolic transformation of a standard ellipsoid (right).

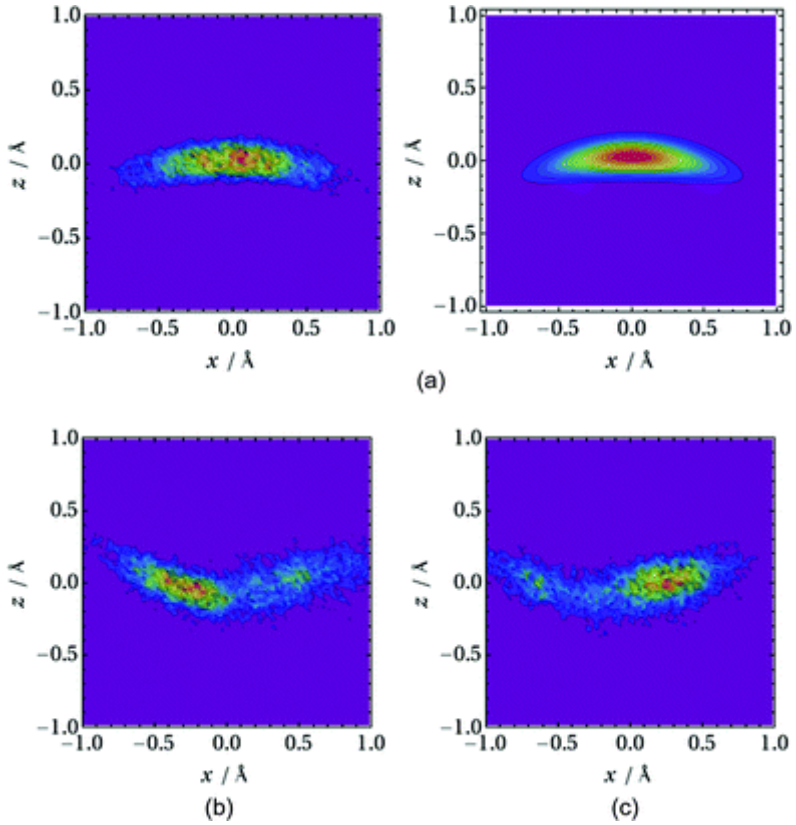

Figure 4. Calculated PDFs for various hydrogen atoms in $(PH_3)_3RuH_4$. With reference to the numbering scheme indicated in Fig. 2 the atoms shown are (a) H(2), with the fit to the parabolic transformation of a standard ellipsoid shown alongside, (b) H(3) and (c) H(4).

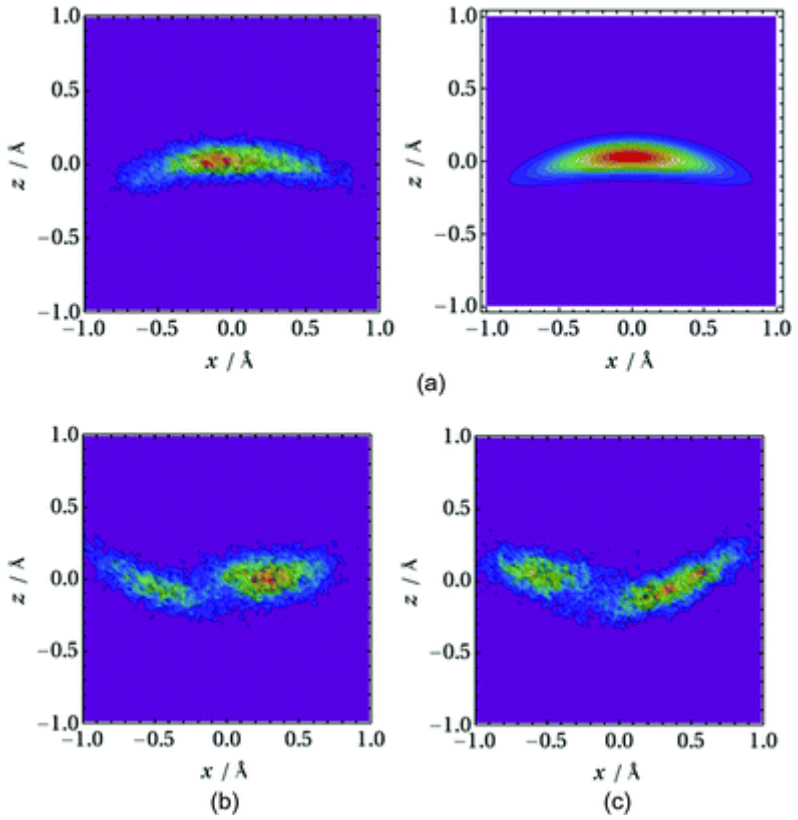

Figure 5. Calculated PDFs for various hydrogen atoms in $(PH_3)_3FeH_4$. With reference to the numbering scheme indicated in Fig. 2 the atoms shown are (a) H(2), with the fit to the parabolic transformation of a standard ellipsoid shown alongside, (b) H(3) and (c) H(4).

The distributions for the η^2-bound hydrogen atoms are shown in Fig. 4(b) and 4(c) and Fig. 5(b) and 5(c) for the Ru and Fe complexes, respectively. From this it is clear that the two hydrogen atoms oscillate between two closely positioned basins on the potential energy surface due to the torsional twist along the M–H_2 bond. The mean positions for these atoms must logically be placed in the middle of the bi-modal surface, but this necessitates that both atoms are positioned practically on top of each other, which results in unrealistically short H–H distances for both complexes (see Table 1). Note this effect has come about because by simply averaging the coordinates of each atom and reporting the distance between their subsequent mean positions we have lost the correlation between the motion for this pair of atoms. However, determining the distance between the mean positions of the two basins does allow reasonable H–H bond distances to be recovered, of around 0.8–0.9 Å for both complexes.

These bi-modal distributions are too complex to fit with our simple parabolic distribution, and serve to highlight the degree of asymmetry observed in these complexes. However, we can quantify the overall degree of curvature by observing that the mean positions of the bi-modal distributions sit on approximately the same radius of curvature as observed for the classically bound hydride atoms. This is shown for the two complexes

in the central images in Fig. 2; thus if we assume that the same librational correction for M–H(2) applies to M–H(3,4) then we can estimate that fitting the atomic PDFs for the H_2 atoms to a harmonic distribution will underestimate the H−H distance by around 0.01 Å, which represents a correction of around 1σ compared to the experimental value reported for the $(Ph_2EtP)_3FeH_4$.

Thus, to summarise, our MD simulations have allowed the direct visualisation of the degree of anharmonicity present in the $(PH_3)_3MH_4$ system. We have successfully fitted classically bound hydride atoms to a curved PDF that results in a significant lengthening in the M–H distances, compared to the standard harmonic PDF approach. The numerical PDFs obtained for the dihydrogen ligand atoms show bi-modal distributions that are too complex to fit to our simple parabolic ellipsoid description. However, a crude estimate of the anharmonic bond distance correction is only of the order of 1σ, which suggests that the experimental error in modelling the H_2 ligand harmonically is actually quite small. Finally, we note that the time-averaged bond distances obtained from the direct extraction of distances from the MD trajectories retain the property of atomic correlation and thus allow those distances most affected by anharmonicity to be easily identified.

Simulated vibrational spectra: Vibrational spectroscopy has played an important role in characterising TM dihydrogen complexes. The $MH_2(H)_2$ unit is expected to give rise to a total of nine vibrational modes, encompassing the H–H stretch, the M–H stretches (ν_s and ν_{as}), various δM–H deformation modes and the M–H_2 torsional mode, but rarely have all modes been characterised experimentally. Indeed, the six modes attributed to the M(η^2-H_2) triangular unit have only been experimentally identified for one complex.[6]

We present our calculated spectra for the three complexes in Fig. 6. They were obtained by Fourier transforming the velocity autocorrelation functions for just the four hydrogen atoms attached to the metal centres. The bands present can therefore be entirely attributed to the MH_4 structural unit. Crucially, we point out that thesespectra take anharmonicity into account. Note, however, that obtaining vibrational frequencies in this way does not result in realistic spectral intensities as although thespectra are mass-balanced the change in dipole behaviour over the course of the MD trajectories has not been factored in. In addition to obtaining the complete MH_4vibrational spectra, we can also extract vibrational information from individual internal structural parameters, such as the M–H bond distances, H–M–H angles, *etc*. This is done by Fourier transforming the autocorrelation function of individual parameters extracted directly from the MD trajectory file. Superimposing the result on the total MH_4 vibrational spectra allows an attempt at band identification to be made.

From experiment it is known that a classic hydride complex would be expected to show *ν*M–H bands in the region 1700–2300 cm^{-1} and deformation δM–H bands around 700–900 cm^{-1}.[6] These bands are present on our simulated vibrational spectrum for $(PH_3)_3OsH_4$ (see Fig. 6). The Os–H distances exist as two pairs, with the outer distances slightly longer than the inner pair (see Table 1). This structural difference is also manifest in

the vibrational spectra, where we assign ν_{as} M–H(1,4) and ν_{s}M–H(1,4) to 2020 and 1865 cm^{-1}, respectively; the corresponding values for the inner pair are 2085 and 2015 cm^{-1}, respectively. The spectrum below 850 cm^{-1} is a challenge to interpret. A cleaner interpretation can be obtained by extracting the vibrational information directly from one of the H···H contacts over the course of the trajectory. This process allows the individual modes responsible for modulating this particular bond distance to be identified. This information [specifically for the H(1)···H(2) interaction] is presented as a red line alongside the OsH_4 spectra in Fig. 6, which greatly aids the eye in locating the remaining five modes at 840, 680, 500, 280 and 105 cm^{-1}. Analysis of the vibrational information obtained over the course of the trajectory for the angles ∠H–Os–H and ∠P–Os–H allow us to assign all of the bands around these peaks to combinations involving all these angles, with the exception of the band around 280 cm^{-1} which we attribute to deformations of ∠H–Os–H only.

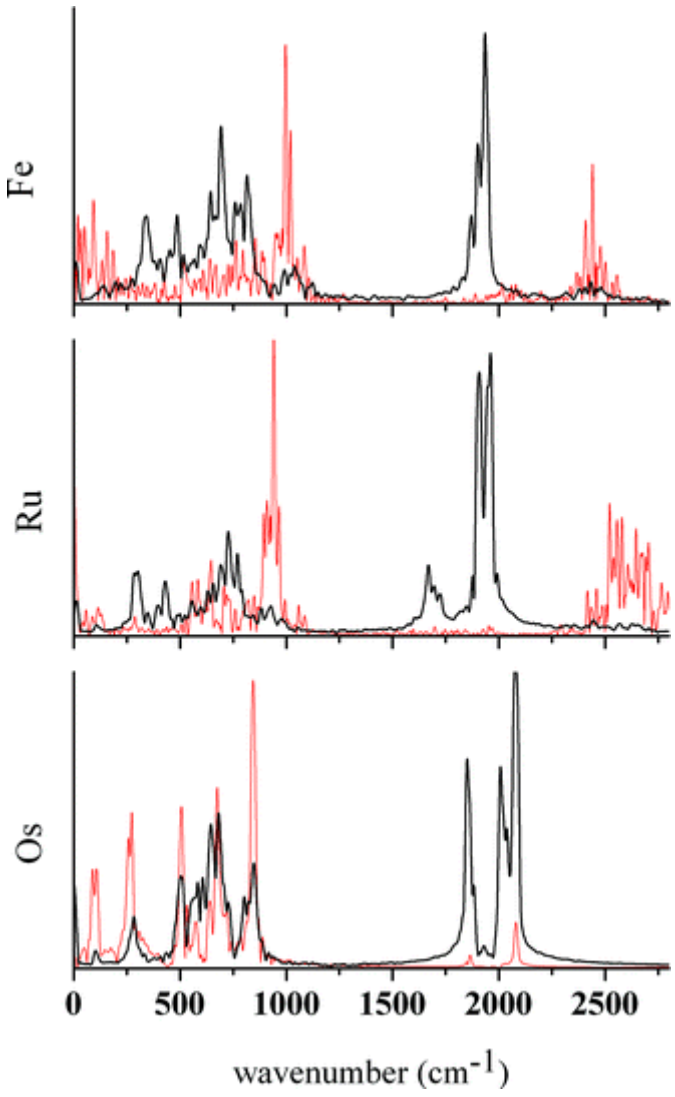

Figure 6. Vibrational spectra for the hydride and dihydrogen ligand atoms present in $(PH_3)_3MH_4$, obtained by Fourier transformations of the velocity autocorrelation functions (black lines) or H–H distance autocorrelation functions (red lines).

The simulated vibrational spectra for the Ru and Fe complexes, also shown in Fig. 6, immediately indicate that these systems are much more anharmonic. The M–H stretching modes for the classically bound hydrogen fall in similar locations as observed for the Os case, at around 1930 cm^{-1} for both complexes. Experiments suggest that the M-(η^2H_2) antisymmetric stretch should appear around 1300–1600 cm^{-1}, whereas the symmetric stretch drops to 850–1000 cm^{-1}.[6] Our results largely concur with these observations, with the pair of values simulated for the Ru complex appearing at 1690 and 885 cm^{-1} and for the Fe complex at 1880 and 1000 cm^{-1}. Evidence for the existence of the H–H stretching modes are present for both complexes but the signals are weak, falling at around 2500–2800 cm^{-1} and *ca.* 2450 $cm^{-1}$for the Ru and Fe complexes, respectively. The signals are much greater amplified in the Fourier transformation H–H distance autocorrelation functions, which show that the vibrational frequencies largely responsible for modulating these distances are, in addition to the H–H stretches themselves, the aforementioned ν_{as}M-(η^2H_2) modes centred at around 880–1000 cm^{-1}. The remaining modes for both complexes are a complex mix of deformation modes, with maxima recorded around 740 and 435 cm^{-1} for the Ru complex and 810, 700, 650 and 500 cm^{-1} for the Fe complex. This shows broad similarities with a vibrational spectrum obtained from inelastic neutron scattering (INS) for the $(Ph_2EtP)_3FeH_4$ complex.[15] Worthy of special mention are the M-(η^2H_2) torsional modes, which due to quantum effects can appear as split peaks on the experimental spectra. INS experiments have assigned this mode to *ca.* 200–350 cm^{-1}; Fourier transforming the autocorrelation functions of these internal parameters gives rise to broad signals for both complexes at around this region, which tally with the absorptions we obtain in the Fourier-transformed velocity autocorrelation spectra.

Fluxional behaviour of $(PH3)_3FeH_2(H)_2$: A curious phenomenon was observed in the MD trajectory recorded for the Fe complex: at around 9 ps the identity of the η^2-bound H_2 spontaneously changed, such that the short H···H contact switched between the hydrogen atom pairs H(1)···H(2) to H(3)···H(4) [see Fig. 7(c) and (d)]. Both structures are otherwise identical, and minimise to the same structure on the underlying potential energy surface. Due to this structural change, a longer trajectory was recorded for this complex in order that sufficient data could be obtained for the numerical PDF analysis presented above. We note that this phenomenon has been reported previously by Van Der Sluys *et al.*,[15] who summarised it as an interaction between the σ_{HH}* orbital and a neighbouring occupied $\sigma_{Fe–H}$ orbital. In this way it has been postulated that a classical tetrahydride intermediate is avoided. However, we note that our $H_2/(H)_2$ transition is somewhat different, in that we observe a flip directly between H(3)–H(4) and H(1)–H(2), rather than the switch from H(1)–H(2) to H(2)–H(3) as presented in the earlier study.

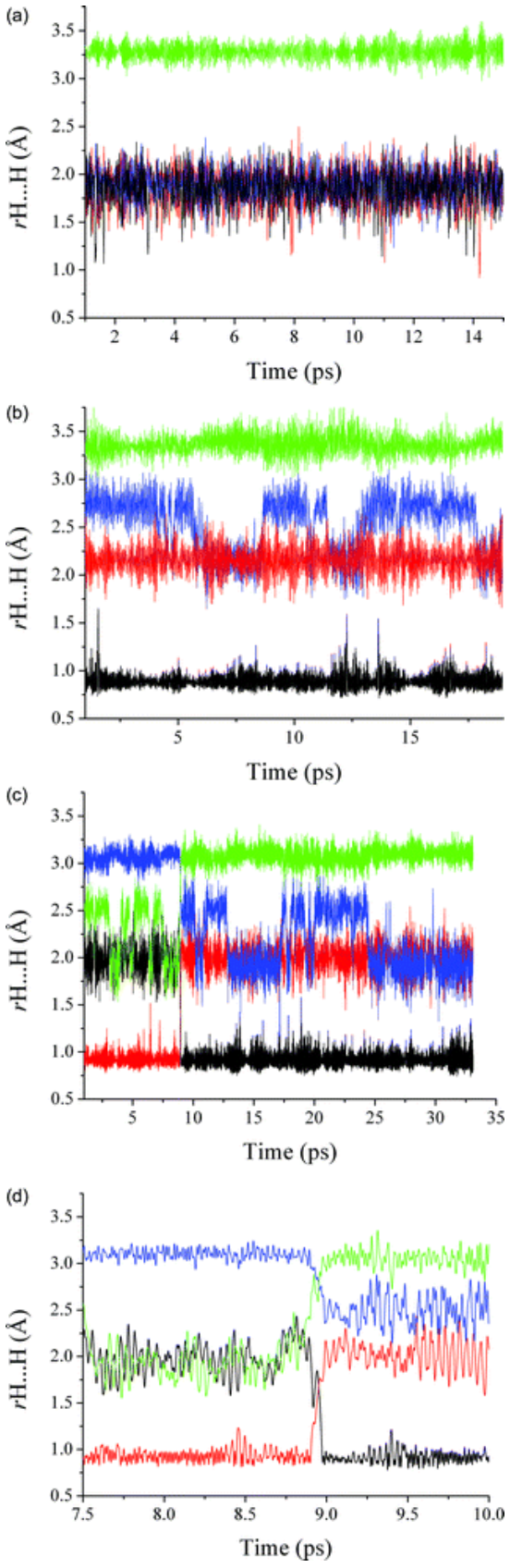

Figure 7. Behaviour of the H···H distances observed in the MD trajectories for the complex $(PH_3)MH_4$, where (a) M = Os, (b) M = Ru, and (c, d) M = Fe.

In an attempt to cast further light on this phenomenon we offer the following observations. Fig. 7 shows the contact information for all four pairs of H···H distances for the three different complexes. With reference to the numbering scheme indicated in Fig. 2, they are H(1)···H(2), H(2)···H(3), H(3)···H(4) (representing the η^2-bound $H_2$for the Ru and Fe complexes) and the long distance H(1)···H(4). We can see that in the case of the Os (classical) complex the three short distances are equivalent, and oscillate around a mean value of *ca.* 1.8 Å. The long H(1)···H(4) distance adopts a steady value of *ca.* 3.3 Å [Fig. 7(a)]. In the case of the dihydrogen complexes, however, the three short distances are now quite different: the H(2)···H(3) distance fluctuates between two steady structures, at around 2.1 and 2.75 Å for the Ru complex, and 2.0 and 2.5 Å for the Fe complex [Fig. 7(b) and (c)] due to rotation of the H_2 ligand. Both complexes display the H(3)···H(4) distance as a bonding interaction at around 0.9 Å. The long H(1)···H(4) distance appears to be slightly shorter in the Fe case (around 3.0 Å, compared to *ca.* 3.3 Å for the Os and Ru complexes).

Thus we observe that for the Fe complex the non-bonding H···H contacts oscillate around shorter values compared to the Ru complex. In all likelihood this plays an important role in the fluxional behaviour of this complex. Before the transition we observe that the non-bonded distances H(1)···H(2) and H(2)···H(3) coalesce [Fig. 7(d)]. The trigger for the transfer event then appears to be the η^2-bound H_2 twisting into the same plane as the classically bound hydrogen atoms, which also undergo rapid fluctuation to conform to a planar system [*i.e.* τH(1)–H(2)–H(3)–H(4) ≈ 0]. The transition then occurs very rapidly, over a timescale of less than 0.15 ps, and all four H···H distances take up their new mean values at exactly the same time. We note that a close to co-planar system is observed on several occasions over the course of the 33 ps trajectory, and yet the transition occurs only once, which indicates that other factors must also be at work. This observation does, however, support the general hypothesis of Van Der Sluys, as the orbital overlap between $\sigma_{Fe–H}$ and σ_{HH}* is of course a maximum when the FeH_4 system is planar. Further analysis of our MD trajectory requires an in-depth analysis of the electron density topology which will be reported in a future publication.

4. Conclusions

This work is a report of a computational study that attempts to quantify the degree of anharmonicity present in the iron triad system $(PH_3)_3MH_4$ (M = Os, Ru and Fe). For each complex we present three sets of M–H and H–H distances: the equilibrium distances, the time-averaged inter-atomic distances, and the distances derived from the time-averaged atomic positions. Calculating the time-averaged inter-atomic separations retains atomic correlation and the tabulated bond lengths show the expected bond-lengthening effect due to Morse-oscillatory behaviour. The distances between the time-averaged positions, which are obtained in a manner similar to standard crystallographic practise, loose this correlation and the resulting values are significantly shorter than their equilibrium partners. This study therefore highlights the problems encountered in studying highly anharmonic systems using standard crystallographic techniques.

The MD simulations also allow for direct visualisation of the atomic PDFs, and we were able to fit the simpler distributions to a parabolic transformation of a thermal ellipsoid requiring only a further two parameters to bend the distribution around two axes. This process resulted in significant lengthening of the M–H bonds, of around 0.01 Å in the case of Os and 0.02 Å for Ru and Fe. While the atomic PDFs for the η^2-bound H_2 ligand showed a rather complex bi-modal distribution we were able to estimate a H–H bond distance correction of around 0.01 Å in both cases.

We also present assigned vibrational spectra for the three complexes, which find very good agreement with experimental results presented for similar complexes. Finally, we report on a spontaneous η^2-H_2 ligand flipping process observed for the Fe complex, the mechanism for which appears to need all atoms in the MH_4 unit to exist in the same plane. Further work on the change of the topology of the electron-density surface through this transition is now planned.

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